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SUMMARY

Titanium carbide coatings were radiofrequency sputtered onto 440C disk with various partial pressures of nitrogen added to the plasma during the first few minutes of deposition. The adherence, friction, and wear properties of these coatings were evaluated with a pin-on-disk apparatus which comprised an AISI 304 stainless-steel rider sliding on the coated 440C disk. The wear and adherence properties of these coatings were superior to coatings applied by other methods such as sputter etching the substrate, oxidizing the substrate, or adding a small oxygen partial pressure during deposition.

X-ray photoelectron spectroscopy and X-ray diffraction analyses showed that the improved adherence was related to the formation of an interference - a mixture of titanium and iron nitrides, which are harder than their corresponding oxides.

INTRODUCTION

Considerable interest in the use of hard coatings for wear resistance has prompted work on various methods of application. A most attractive method is rf sputtering. Many different hard refractory compounds have been studied for wear resistance purposes when applied by sputtering (refs. 1 and 2). These studies have shown that coatings applied by sputtering can provide wear protection and in many cases low friction.

Most coatings are, however, limited not by coating properties but rather the adherence of those coatings to the substrates. Failures have been generally observed to occur at the coating-substrate interface.

Previous work (ref. 3) showed that for certain refractory types of material (e.g., TiC, $MoSi_2$, and Mo_2C) significant improvement in adherence could be obtained if the steel surface was oxidized before coating. Steel surfaces that had been furnace treated to produce thin iron-oxide layers before being sputter coated performed better in friction and wear experiments. Depth profile analysis of several interfaces suggested that the improvements in adherence were related to the formation of a "mixed oxide" interface comprising iron oxide from the substrate and oxides of the constituents of the refractory compound being sputtered.

While furnace treating steel to promote oxide growth may appear easy, it has the disadvantages that (1) the temperatures necessary for oxide formation may be high

enough to soften the steel or otherwise degrade its physical properties and (2) for any manufacturing process any additional processing requirements either in terms of time or equipment tends to make the process more expensive and, thereby, less attractive.

Greene and Pestes (ref. 4) have also studied the adhesion of sputtered titanium carbide (TiC) films on steel and found improved adherence when oxides are formed at the interface. Their approach was to introduce a small percentage (2 percent) of oxygen into the argon plasma during deposition to promote the formation of a graded interface, which reportedly measures 1250 Å in width. However, questions concerning the validity of these measurements have been raised (ref. 5). Additionally, recent work by Pepper (ref. 6) has shown that a small nitrogen partial pressure during the first few minutes of sputter deposition promoted adherence as measured in shear strength experiments for metal-ceramic couples.

The objective of this investigation was twofold: first, to determine if additions of oxygen during sputter deposition of TiC was as effective in promoting adherence as was substrate oxidation; and, second, to determine the influence of a nitrogen partial pressure in the argon sputtering plasma on the adherence, friction, and wear properties of sputtered TiC coatings on 440C steel.

Sputtered TiC coatings were deposited under a variety of conditions onto 440C steel friction specimens. The coatings were analyzed by X-ray diffraction and X-ray photoelectron spectroscopy (XPS) in addition to being evaluated in pin-on-disk experiments.

APPARATUS AND PROCEDURE

Specimen Preparation

The 440C bearing-steel disk and 304 stainless-steel pin specimens were all mechanically polished in the same manner. The pins and disks were abraded on silicon carbide papers down to 600 grit. Then they were polished with a 3-micrometer diamond paste and lapped with 1-micrometer alumina. After lapping, the disks were rinsed with alcohol, dried and, inserted into the radiofrequency (rf) sputtering apparatus.

Radiofrequency Sputtering

The sputtering was done in a commercial, radiofrequency diode apparatus (fig. 1), which operates at 13.56 megahertz. The sputter materials were hot-pressed, disk-shaped (15.2 cm diam), compacts, which were commercially purchased. The compact, or target as it is called when mounted, is cemented with a silver conductive epoxy onto

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a copper backing plate (0.60 cm thick). The copper backing plate is mounted onto a water-cooled rf electrode (also 15.2 cm diam). The specimen to be coated (i.e., substrate) is placed 2.5 centimeters directly below the target on an electrically insulated block. The insulated block sits on the grounded substrate table. (The target and the grounded table constitute the rf diode.) An additional voltage from 0 to -1500 direct-current volts may be applied directly to the specimen either for specimen cleaning by direct-current sputter etching or for biasing the specimen during film deposition and growth. The entire substrate table can be rotated so that the disk specimen may be moved out from under the target. The target can thus be cleaned without contaminating the specimen. If desired, the disk could be cleaned by sputter etching during this time.

The entire diode system is contained in a 45-centimeter-diameter, glass bell jar. The system is mechanically forepumped and oil diffusion pumped through a liquid-nitrogen-cooled baffle. Two variable leak valves are also attached to the system: One valve regulates the flow of high purity argon (99.9995 percent); the other valve controlled the flow of either the oxygen or nitrogen, depending on which gas cylinder was attached to the bleed in line.

Before deposition, the target was cleaned by rf sputtering until little pressure rise due to outgassing occurred. After the target was cleaned, the disk specimen was sputter etched (cleaned) for 15 minutes at -1200 volts. After this cleaning, the argon leak valve was closed, and the system pumped to the base pressure 1.33×10^{-4} pascal ($\sim 10^{-6}$ torr). At this time either oxygen or nitrogen was bled into the system to whatever partial pressure was desired. Once the oxygen or nitrogen partial pressure was set (typically in the range 1.33×10^{-3} to 6.65×10^{-2} pascal (1×10^{-5} to 5×10^{-4} torr)) the argon valve was again opened and the total pressure raised to the sputtering pressure of approximately 2.7 pascals (20 μm of mercury).

The voltage on the disk was then reduced to -500 volts for biasing; the specimen was rotated back under the target; and deposition begun. After the first 2 minutes of deposition, during which time the critical interface is formed, the valve controlling the oxygen or nitrogen flow was closed, the sputtering ambient again reduced to pure argon, and the deposition continued without interruption. The power density was 1.64 watts per square centimeter, and deposition times were from 5 to 40 minutes; the shorter deposition time being used for making of XPS samples, where thick specimens were not required. For friction and wear testing, coatings were approximately 3000 Å in thickness. Thicknesses were measured by surface profilometry of a deposition step.

Friction and Wear Testing

The rf-sputtered films were evaluated in a pin-on-disk apparatus (fig. 2) of the type often used for solid-film lubrication evaluation. The flat, 6.4-centimeter-

diameter disk is mounted on the end of a rotating shaft. The disk specimen is a type 440C bearing-steel disk (58 to 60 R_C) that has been rf-sputter coated with one of the experimental materials. Loaded against the surface of the disk is a 0.476-centimeter-radius pin of AISI 304 stainless steel. The pin is mounted in a holder on the end of, and perpendicular to, a gimbal-supported arm. The pin is loaded against the surface of the disk by weights hung on the arm halfway between the pin and the gimbal. Normal loads of 2 to 15 newtons (200 to 1500 g_{force}) were used. The end of the arm opposite the pin holder is attached to a strain-gage bridge, which measured the frictional force. A new pin specimen was used for each experiment. The entire apparatus is enclosed in a clear plastic box. A constant flow of dry nitrogen (<20 ppm H_2O) is maintained in the box before and during friction experiments in order to minimize environmental effects.

The experiments reported herein were each conducted for 30 minutes at a constant speed of 25 centimeters per second. After the friction testing, the disks were examined by optical microscopy and surface profilometry to determine the extent, if any, of film wear or spalling from the 440C substrate. Film spalling was evident on the surface profile tracing by the appearance of sharp, vertical-sided, flat-bottomed cross sections, which are characteristic of a brittle film spall. Friction coefficients reported are averages over the entire 30-minute running time.

The pin-on-disk configuration provides extremely high contact stresses, in contrast to the conforming type of contact. The initial Hertzian stress for the uncoated disk contacted by the 304-stainless-steel pin at a 2-newton load was 39.13 kg/mm^2. Any coating that performs well under such extremes would probably perform as well or better under less severe conditions. Thus, in this respect, the pin-on-test can be regarded as an upper limit screening test for these coatings.

X-Ray Photoelectron Spectroscopy

The principles of XPS are detailed in reference 3. The apparatus used here consists of a commercial electron analyzer and X-ray source in a vacuum system designed to accommodate a variety of samples. The system is a stainless-steel, bakeable, ultrahigh vacuum system. It is ion pumped, and it incorporates a titanium sublimation pump. An ion gun in the system was used to gradually sputter away the sample surface and determine the composition as a function of depth. The gun used argon ions of 5-keV energy. The ion gun was equipped with deflection plates, which permitted the beam to be scanned in a raster pattern while sputtering. Thus, a uniform sputtering rate was obtained over an area larger than the area analyzed by XPS. The sputtering rate was measured on a sputtered TiC coating deposited on a glass slide and on a 550-Å gold

film evaporated onto a silicon substrate. In both cases the sputtering rate was 4 to 5 Å per minute. The width of the gold-silicon interface, measured by extrapolating the steepest part of the gold peak height versus depth curve was 125 Å, which is taken to be the depth resolution characteristic of this study (ref. 3).

After a film had been sputter deposited, the disk was rinsed with ethyl alcohol and mounted in the spectrometer vacuum chamber. The base pressure in the chamber was allowed to reach about 5×10^{-7} pascal. The first X-ray photoelectron (XP) spectra were then obtained. Then, with the ion pump off, the pressure was raised to 6.7×10^{-3} pascal with argon, and the ion gun operated for an interval. The chamber was then pumped back to about 5×10^{-7} pascal and the XP spectra were again recorded. This procedure was continuously repeated with sputtering times varying from 5 to 30 minutes, depending on how rapidly the spectrum was changing, until the interface was completely sputtered through.

The positions of peaks in the XP spectrum identify the elements present in the surface of the sample and give some information about the oxidation states of those elements. The sizes of the peaks are related to the amounts of the corresponding elements.

RESULTS AND DISCUSSION

Friction and Wear Test Results

Titanium carbide coatings were applied to several 440C disk specimens under a variety of conditions so that comparisons of the effectiveness of nitrogen and oxygen partial pressures and substrate preoxidation could be made. A variety of oxygen and nitrogen partial pressures were used. The results presented in figures 3 and 4 represent the best performance that was obtained for that particular gas. The oxidized substrates were prepared as previously reported (ref. 3) by furnace heating to 340° C for 18 to 20 hours. This treatment produced a thin, reddish oxide, but did not soften the 440C disk. Also shown for comparison in the figures are data for coatings applied directly to sputter-etched surfaces without any oxygen or nitrogen partial pressure. The data of figure 3 were taken at a load of 2 newtons, and those from figure 4 at 5 newtons.

These experiments not only measure the friction and wear properties of the TiC coatings but also indirectly measure coating adherence. The combination of the 304-stainless-steel rider and a 440C disk, is very sensitive to spalling, or breaking off, of the coating. When the coating begins to fail by spalling, the friction and wear generally increases rapidly, due to an acceleration of film failure by a mechanism that is summarized and illustrated schematically and photographically in figures 5 and 6.

The transfer of the softer stainless to the exposed 440C surface causes a buildup of shear stresses at the film interface due to the high localized friction force between the 304 rider and the transferred material. With the harder, 440C rider, the transfer to a spalled region is much less likely to occur and coating life would be longer.

Both nitrogen and oxygen partial pressure provide some improvement over the sputter-etched-only values; however, the oxygen partial pressure technique did not yield wear results as good as furnace oxidation did. At a load of 2 newtons (fig. 3), although the average friction coefficient is low, spalling during the latter minutes of running, resulted in the higher rider wear volume. The coatings on the oxidized 440C disk and the coating prepared with an initial nitrogen partial pressure exhibited comparably low friction and wear.

At the higher, 5-newton load (fig. 4), only the sample prepared with nitrogen ran the entire 30 minutes without spalling. All other coatings, regardless of how prepared, failed, resulting in high friction and rider wear.

Several coating specimens prepared with various nitrogen partial pressures were tested to ascertain the optimum amount of nitrogen for best friction and wear performance. The results are shown in table I. Film failure is listed for coatings that spalled before the end of a 30-minute test at a load of 10 newtons. Coatings prepared at partial pressures of 1.3×10^{-2} and 6.6×10^{-2} pascal (~0.5 to 2.4 percent of the plasma) ran the entire 30 minutes without any evidence of coating failure. In fact, both of these coatings ran without failure during the 15-newton-load tests and still exhibited low friction ($\mu = 0.32$). These conditions represent extremes in sliding contact, that is, Hertzian stress of 75 kg/mm^2 (110 000 psi), and any nominally brittle material that can perform under these conditions would be very attractive for less demanding applications.

Coating Analysis

In previous work (ref. 3) the role of interfacial oxides between the sputtered refractory compound and the steel substrate or adherence, friction, and wear was studied. This work showed that, when oxides of both the constituent refractory compound element and the iron substrate were formed in mixed layers, significant improvements in adherence, friction, and wear resulted. Similar effects were anticipated when nitrogen was deliberately introduced during the crucial interface formation. In the case of sputtered TiC, it was expected that some of the titanium at the interface would react to form titanium nitride (TiN). In addition, the iron in the substrate could form a nitride. These two nitrides, mixed together, could act to more strongly bond the growing TiC coating. To verify if these events occurred, both X-ray diffraction and X-ray

photoelectron spectroscopy were used to analyze coatings applied with a nitrogen partial pressure.

X-Ray Photoelectron Spectra

The N(1s) XPS peak of a standard sample of pure bulk TiN occurs at 396.8 eV. A 440C disk was then prepared as it would be for coating. After sputter cleaning in argon, the disk was biased at -500 volts and exposed to nitrogen (0.5 percent) containing argon for 2 minutes. The rf power was off, however, so no TiC was deposited. This disk was then analyzed by XPS. The N(1s) XPS peak from this specimen was at 394 eV. When the treated 440C disk was sputter etched to a depth of 1000 Å, its 394 eV N(1s) peak was unchanged in height or position. Although there is no discernible change in the iron spectrum, the fact that the nitrogen persists to such a depth, far beyond what would be expected from ion implantation, indicates the formation of an iron nitride. The ASTM powder diffraction file lists four possible iron nitrides: Fe_3N, γFe_4N, ζFe_2N, and εFe_3N-Fe_2N (ref. 7). It is concluded that the 394-eV N(1s) peak is due to one or more of these.

Figure 7 shows how the N(1s) peak changes during depth profiling a disk coated with TiC using nitrogen as was done for the friction experiments. Unlike the friction test samples, however, this disk was deliberately exposed to the argon-nitrogen plasma for three or four times longer than usual in order to emphasize the nitrogen peak for XPS analysis. The top spectrum was taken after sputter etching into the film bulk but not near the interface. Only TiN (396.8 eV) is present. The second spectrum was obtained after sputter etching to the interfacial region. It clearly shows the presence of both TiN (396.8 eV) and iron nitride (394 eV). The last spectrum recorded when the interface had been sputtered through shows only the N(1s) peak from the iron nitride (394 eV).

Figure 8 is a depth profile of the titanium carbide-steel interface formed with a nitrogen partial pressure (of approximately 1.3×10^{-2} Pa) during the first 2 minutes of deposition. The iron, titanium, oxygen, and nitrogen (396.8 eV, TiN) peak intensities are plotted. The vertical scale is arbitrary since in XPS different elements have different cross sections so unless corrected, direct comparisons of the intensities are not valid. Two things are, however, clear from the figure. First, there is a significant increase in nitrogen, which reaches its maximum at the same time the iron peak intensity is growing the most rapidly. This maximum is likely related to the 2-minute interval when the nitrogen valve is open. When the valve was shut, the nitrogen peak decreases to some equilibrium value associated with the bulk film. Second, the interface is very sharp, only about 200 Å wide. Apparently, then, the improved adherence

is not due to the formation of a broad interface.

Figure 9 is a plot of the 396.8-eV nitrogen peak height and the ratio of carbon to titanium peak heights across the interface. Also shown on the figure is the ratio of carbon to titanium in a bulk calibration standard.

Clearly, the ratio of carbon to titanium drops in correspondence to the increase in nitrogen. This certainly suggests that if stoichiometry is maintained for TiC, then some of the titanium must be in the form of TiN. This also suggests that the carbide and nitride are mixed in this interfacial region. If the TiC stoichiometry is maintained, the carbon to titanium peak height ratio allows a calculation of the fraction of titanium present as the carbide. The remainder presumably is the nitride. In this particular case there is 13 percent TiN in the film itself, with a maximum of 41 percent at the interface. These values are typical of several films examined. These composition estimates were checked by using them to calculate the height of the 396.8-eV N(ls) peak to be expected using the nitrogen to titanium peak height ratio obtained from the TiN standard. The value obtained agrees well with the observed 396.8-eV N(ls) peak height.

X-Ray Diffraction Analysis

After the XPS analysis, three, thick (~1 μm), sputtered titanium carbide samples were prepared for X-ray diffraction studies: The first was prepared with -500-volt bias to maximize stoichiometry by minimizing titanium oxide impurities; the second was prepared without bias, thus, containing a large amount of oxide; and the third was deposited with a partial pressure of nitrogen (1.3×10^{-2} Pa) the entire time. This latter sample was meant to simulate the type of sputtered coating that formed at the interface on friction and wear coatings during the first 2 minutes of deposition. All three samples were examined for structure and orientation, and measurements made to determine the lattice parameter.

The normal diffraction pattern for bulk TiC yields the maximum reflection for the (200) planes and an 80 percent intensity reflection for the (111) planes with increasingly smaller intensity peaks for (220), (113), and so forth (ref. 8). For the biased sample and the nitrogen partial pressure sample, only the (111) reflection could be observed. For the unbiased sample a weak (200) reflection at about 17 percent of the (111) reflection intensity was also observed. These findings are in accord with Mah, et al. (ref. 9), who also found (111) to be the strongest reflection from sputtered TiC coatings. Those authors also observed numerous higher order reflections (e.g., 220, 311, 322) that were not detected in these studies. This is likely due to the greater thickness of their samples (5 μm) in contrast to ours (1 μm).

The (111) plane is the highest atomic density plane for the face centered cubic (fcc) structure, and the preferred orientation of the sputtered films with the (111) planes parallel to the interface may be an important reason why these coatings have such good friction properties. It was of interest to determine if either nitrogen or oxygen (unbiased sample) made any difference in the preferred orientation of these coatings. Therefore, each of the three samples was mounted on a goniometer stage and the intensity of the (111) reflection recorded as a function of the tilt angle φ as shown in figure 10. The data are plotted as a normalized ratio to the substrate iron (111) reflection for easier comparison. Both the biased sample and the nitrogen sample behave identically. The coating is highly oriented with the (111) planes parallel to the surface. The intensity falls off rapidly as the sample is tilted, so after 14° the reflection is almost gone. The unbiased sample containing the oxide, on the other hand, while still showing a preferred parallel (111) orientation, does not drop off as sharply indicating more randomness in the orientation.

Since other reflections were not observed, a silver standard was used to determine the lattice parameter. Silver paint, like that used for repairing electronic circuit boards, was thinly spread over the coated surface to provide a second reflected peak. Figure 11 shows the nitrogen partial pressure sample contrasted with the bias prepared sample, and figure 12 shows the unbiased (oxidized) sample also contrasted with the bias prepared sample. The values of a_O were larger than for bulk TiC or TiN.

Both TiC and TiN have the same fcc structure, and a substitutional alloy of both will have a lattice parameter that varies nearly linearly from that for pure TiC to that for pure TiN (ref. 10). The normal difference between the lattice parameter of TiC and TiN is 0.088 Å, with TiN having the smaller parameter because of the smaller atomic size of nitrogen (ref. 11). The 2θ shift between the location of the (111) reflection for the biased sample and the nitrogen partial pressures sample is 0.56° for Cu Kα radiation, which converts to a d spacing difference of 0.066 Å. Assuming linearity of the parameter, this implies the samples are approximately 25 percent TiC and 75 percent TiN.

The sample prepared without bias is also shifted (0.42°) to a higher 2θ angle, indicating a smaller lattice parameter. The shift is again consistent with the smaller oxygen atom replacing carbon atoms in the lattice. Since there are numerous oxides of titanium with several structures, no attempt to estimate composition from the X-ray data was made.

It is useful to be able to estimate the concentrations of the various constituents at the coating steel-interface. Using the approximation obtained from X-ray data as a check, a self-consistent analysis of the thick nitrogen partial pressure sample was done with XPS, using the carbon to titanium ratio as described above. The analysis determination was that 65 percent of the coating was TiN. This is in reasonably good

agreement with the X-ray diffractions data value of 75 percent. A good estimate of the amount of TiN in the thinner friction and wear samples coatings, both in the bulk film and at the interface, can be obtained in a similar manner. The results for two different samples are shown in table II. No estimates of iron-nitride concentrations were made because no standard was available for measurement.

The overall picture that is described by the sum of the various analyses, then, is that the addition of nitrogen to the sputtering plasma causes the metal surface to become nitrided and for some of the TiC to be converted to TiN at the interface, the amount being about 40 percent for a partial pressure of nitrogen, which is about 1/2 percent of the total sputtering ambient. These nitrides co-exist and are mixed to some degree. The fact that the adherence and the friction and wear behavior is markedly better than for coating applied on oxidized surfaces or with an oxygen partial pressure may be due to the better bonding between the nitrides present at the interface. The better bonding is likely a reflection of the higher strength that TiN has in contrast to TiO_2 (e.g., hardness of 2450 kg/mm^2 versus ~500 kg/mm^2 (refs. 10 to 12)) and that iron nitride has in contrast to iron oxide.

SUMMARY OF RESULTS

Friction and wear evaluations of sputtered titanium carbide coatings and X-ray photoelectron spectroscopy and X-ray diffraction analyses yielded the following results.

1. The addition of a small nitrogen partial pressure (0.5 percent) during the initial stages of deposition (interface formation) yielded coatings with superior adherence and friction and wear properties in contrast to coatings applied to oxidized surfaces or with an oxygen partial pressure instead of nitrogen.

2. The improvement in adherence is related to the formation of an interface containing both titanium nitride and iron nitride.

3. X-ray diffraction showed the rf sputtered TiC coating done with a nitrogen partial pressure to have a preferred orientation with the densest (111) planes parallel to the surface. In contrast, samples done with oxides present were more random in orientation.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, August 29, 1978,
            506-16.

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TABLE I. - WEAR PERFORMANCE AT DIFFERENT

NITROGEN PARTIAL PRESSURES

Nitrogen partial pressure, Pa	Percent of plasma	Friction and wear behavior at 10-N load
6.6×10^{-3}	0.25	Film failure
1.3×10^{-2}	.50	Smooth low friction $\mu = 0.35$
6.6×10^{-2}	2.5	Smooth low friction $\mu = 0.33$
1.3×10^{-1}	5	Film failure
6.6×10^{-1}	2.5	Film failure

TABLE II. - XPS ANALYSIS RESULTS

Film	Percent TiN in film	Percent TiN at interface
1	13	41
2	18	37
[a]3	65	--

[a]Sputtered with nitrogen throughout.
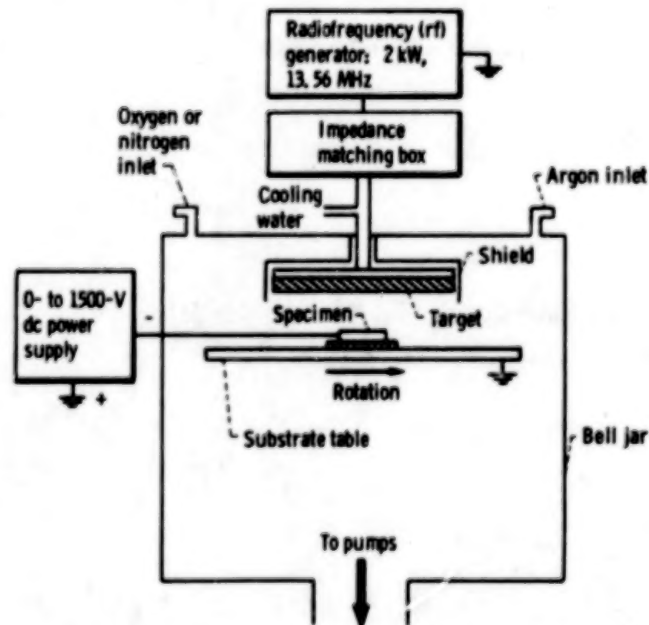
Figure 1. - Schematic of radiofrequency sputtering apparatus.
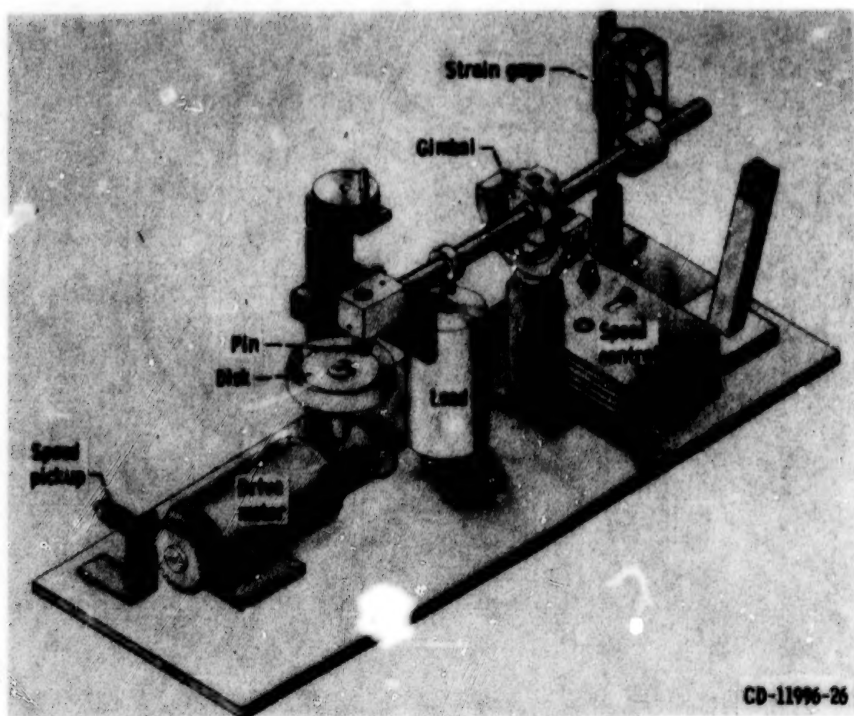
Figure 2. - Pin-on-disk friction and wear tester.
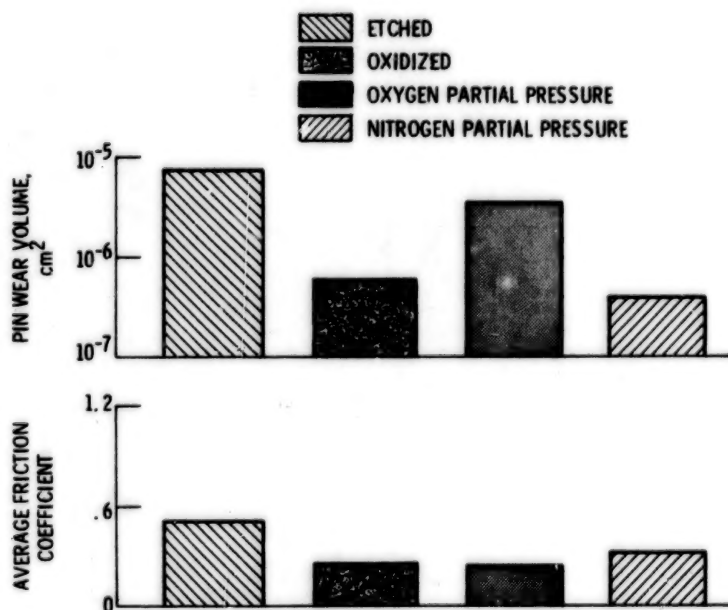
Figure 3. - Pin wear volume and friction coefficient for titanium carbide, rf-sputtered coatings on 440C substrates. Load, 2 newtons; sliding velocity, 25 centimeters per second; nitrogen atmosphere; test duration, 30 minutes; AISI 304 stainless steel rider.
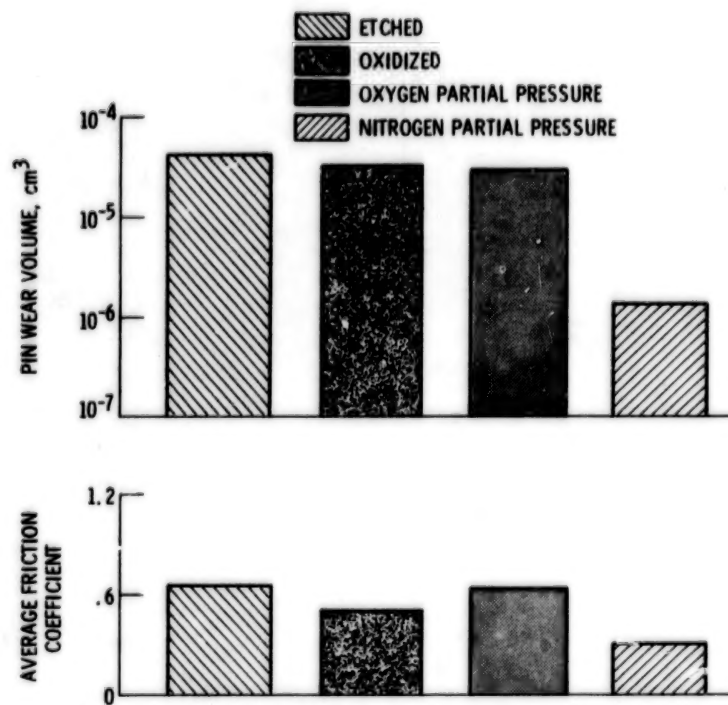
Figure 4. - Pin wear volume and friction coefficient for titanium carbide, rf-sputtered coatings on 440C substrates. Load, 5 newtons; sliding velocity, 25 centimeters per second; nitrogen atmosphere; test duration, 30 minutes; AISI 304 stainless-steel rider.
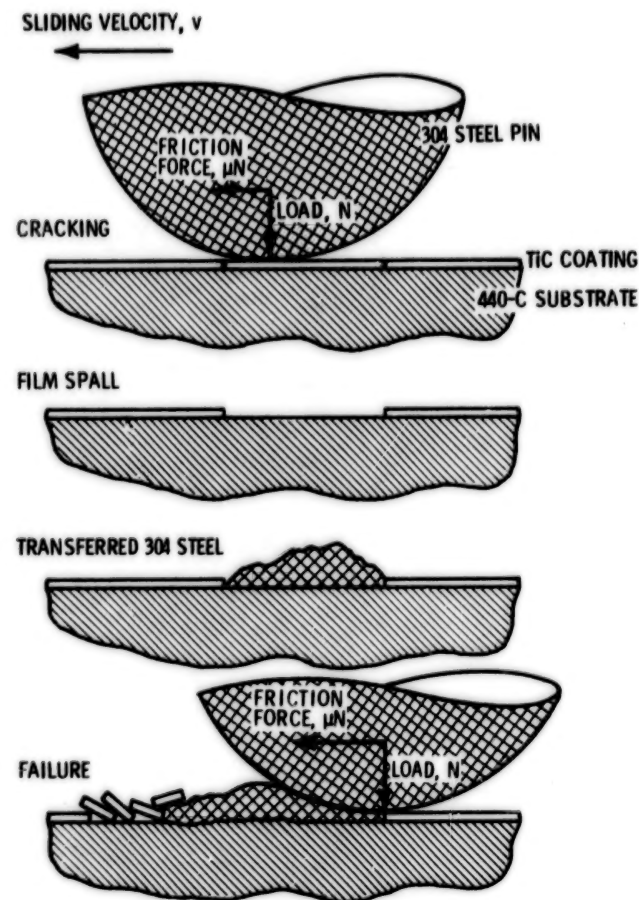
Figure 5. - Illustration of progressive coating failure for AISI 304 stainless-steel pin sliding on rf-sputtered, titanium carbide coated 440C disk.

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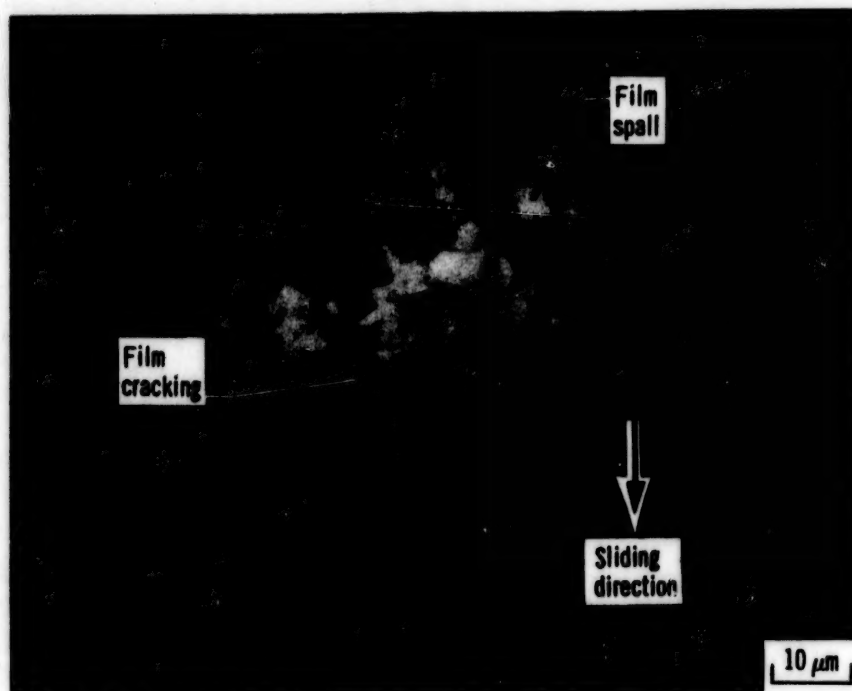
Cracking and spalling.
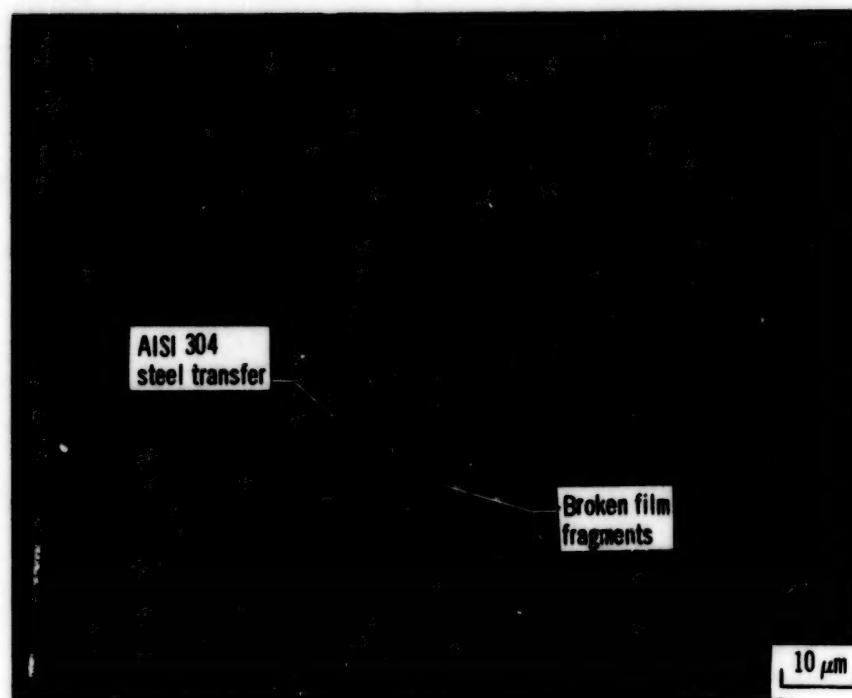
AISI 304 transfer and film failure

Figure 6. - Photomicrographs of wear track on rf-sputtered TIC coated 440C disk.

(a) Coated 440C bulk coating.

(b) Coated 440C interface.

IRON
NITRIDE

(c) Coated 440C substrate.

ELECTRON BINDING ENERGY, eV
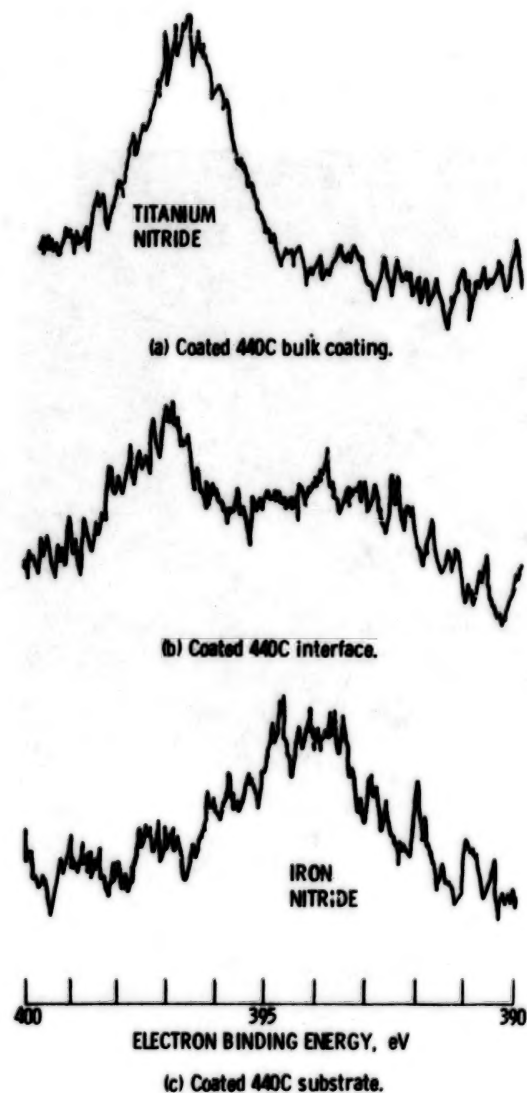
Figure 7. - Nitrogen XPS peaks for 440C disk exposed to
and rf-sputter coated in argon plasma containing ni-
trogen partial pressure of 1.3×10^{-2} pascal. Bias,
-500 volts.
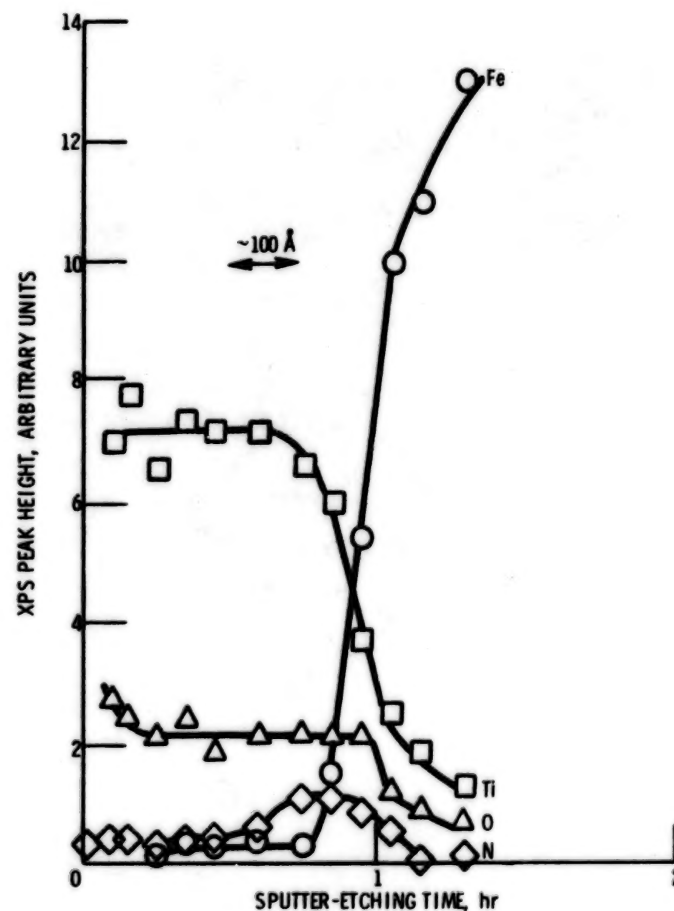
Figure 8. - Depth profile of rf-sputtered titanium carbide coating;
1.3×10^{-2}-pascal partial pressure during first 2 minutes. Bias,
-500 volts.

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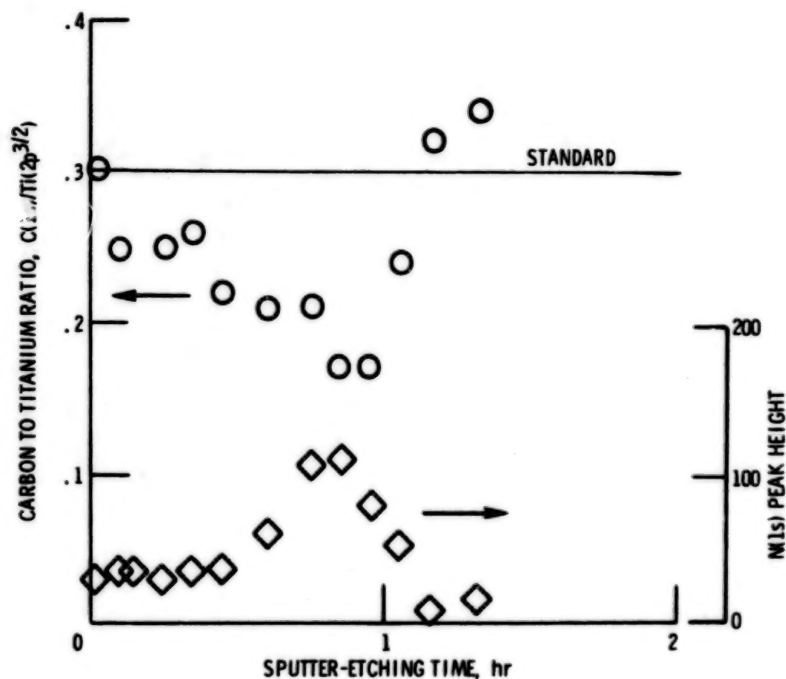
Figure 9. - Variation of carbon to titanium ratio and nitrogen peak heights as function of sputtering depth for rf-sputtered titanium carbide coating; 1.3×10^{-2}-pascal nitrogen partial pressure. Bias, -500 volts.
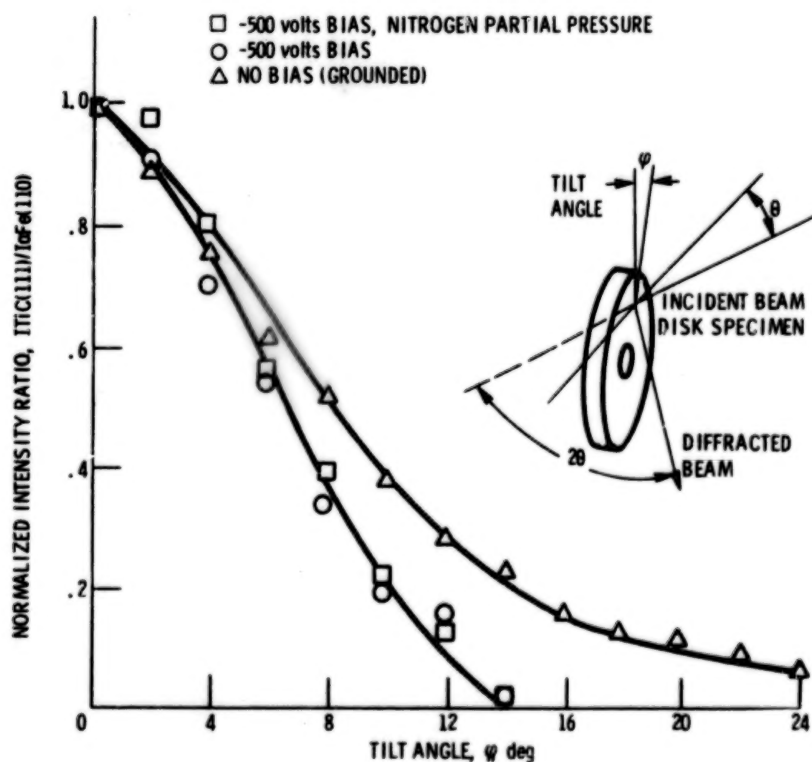
Figure 10. - Variation of TiC(111) reflection intensity ratio with αFe(110) (substrate) for coatings sputtered under three conditions.
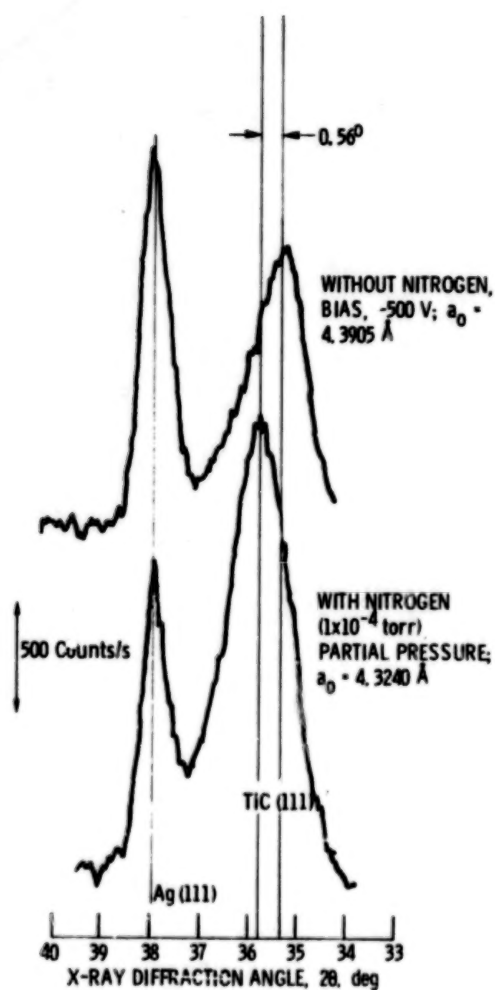
Figure 11. - Shift of TiC (111) reflection for rf-sputtered TiC with and without nitrogen partial pressure. Bias, -500 volts; duration of deposition, 120 minutes; copper Kα radiation, 1. 63 watts per square centimeter.
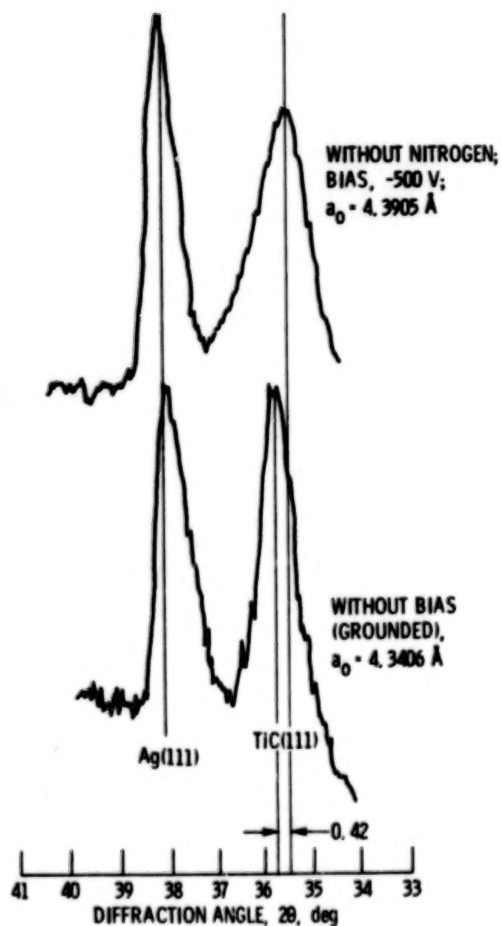
Figure 12. - Shift of TiC (111) reflection for rf-sputtered TiC with and without substrate bias voltage. Deposition, 120 minutes; copper Kα radiation, 1. 63 watts per square centimeter.

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16. Abstract

Friction and wear experiments on 440C steel surfaces that had been rf sputtered with titanium carbide when a small percentage of nitrogen was added to the plasma were conducted. X-ray photoelectron spectroscopy and X-ray diffraction were used to analyze the resultant coatings. Results indicate that the small partial pressure of nitrogen (~0.5 percent) markedly improves the adherence, friction, and wear properties when compared with coatings applied to sputter-etched surfaces, oxidized surfaces, or in the presence of a small oxygen partial pressure. The improvements are related to the formation of an interface containing a mixture of the nitrides of titanium and iron, which are harder than their corresponding oxides.

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